# Soft X-ray Probe of Bulk Bandgaps in Divalent Hexaborides

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## INTRODUCTION

The discovery of weak itinerant ferromagnetism in certain divalent hexaborides [1] provides strong motivation to determine the underlying electronic structure giving rise to the metallic carriers. One possibility predicted by LDA band calculations [2] and supported by the interpretation given to magneto-oscillatory studies [3] is a semi-metallic band overlap at the X-point of the cubic Brillouin zone, the absence of which would render stoichiometric material to be insulating. Several theoretical discussions of excitonic insulator origins of the novel ferromagnetism [4] presume the existence of such an overlap. However, a recent quasiparticle band calculation [5] that includes a GW self energy correction, instead predicts $CaB_6$ to be a semiconductor with a 0.8 eV band gap at the X-point.

Such an X-point band gap (>1 eV) is observed in angle resolved photoemission (ARPES) of $CaB_6$, $SrB_6$ and $EuB_6$ [6] providing strong experimental proof of this new semiconducting model for the divalent hexaborides. Reported here are bulk sensitive soft x-ray emission and absorption data (SXE and XAS, respectively) that provide additional proof of the existence of this semi-conducting bandgap complementary to the k-dependent band structure information revealed by ARPES. Also consistent with ARPES, the SXE/XAS measurements imply that the chemical potential is at the bottom of the conduction band indicating the presence of excess electrons arising from nonstoichiometric defects. This situation would be consistent with a picture in which the novel magnetic moments in divalent hexaborides are carried by boron vacancies [7]

## EXPERIMENT

Single crystal hexaboride samples were grown from an aluminum flux using powders prepared by boro-thermally reducing cation oxides. Soft x-ray emission and absorption experiments were performed at the ALS Beamline 8.0.1 using the Tennessee/Tulane grating spectrometer. The experimental emission and absorption spectral resolutions were $\approx$0.35 eV and $\approx$0.1 eV, respectively. SXE at and above the B K-edge threshold, is used as a probe of the occupied boron 2p partial density of states. X-ray absorption, a probe of the unoccupied states, was measured both with total electron yield (TEY) as a function of photon energy and also with partial fluorescence yield (PFY) with the detection window covering the entire valence band emission. Differences between TEY and PFY signals arise from differing attenuation lengths and the experimental geometry which was set to 60° incidence excitation and 30° grazing emission relative to the sample surface. Absolute PFY energies were calibrated to published TEY spectra of the hexaborides [8] and SXE spectra were calibrated to the excitation energy using an elastic scattering peak in the emission spectra.

## RESULTS

Fig. 1 shows a representative data set of soft x-ray emission and absorption at the boron K-edge for the divalent hexaborides. Data very similar to that shown here for $CaB_6$ was also obtained for $SrB_6$, $EuB_6$, and $YbB_6$. Fig. 1(a) compares the two methods of measuring x-ray absorption, TEY and PFY. TEY, a measurement of the sample current, exhibits a sharp peak at $\approx$194 eV corresponding to a well-known B 1s→2p $\pi^*$ transition [8] which in part arises from surface layer

oxidation of the air-cleaved sample. Also the absolute TEY signal exhibits a high background (removed in Fig. 1(a)) with declining slope due to the presence of lower energy absorption edges. In contrast, the PFY signal, a measure of valence emission intensities integrated over the energy window shown in Fig. 1(b), does not exhibit the sharp TEY absorption peak due to a greater bulk emission sensitivity. Also the valence band PFY signal inherently has zero pre-threshold intensity and hence is preferred over TEY for careful measurement of the threshold region. The PFY spectrum for $CaB_6$ shows a weak step-like threshold onset at 188.0 eV (highlighted in the logarithmic scale inset to Fig. 1(a)). We interpret the half-step intensity of this threshold onset in the PFY spectrum as the energy position of the chemical potential in the conduction band.
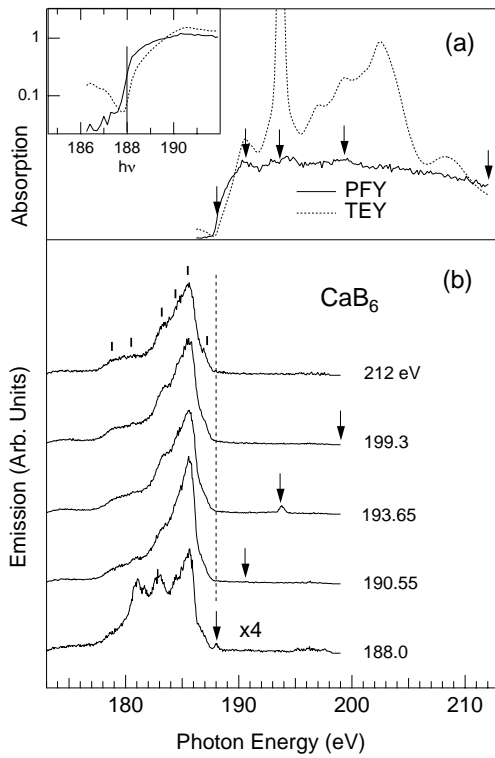


Figure 1. Soft x-ray absorption (TEY, PFY) and emission (SXE) boron K-edge data set for $CaB_6$. Arrows and values indicate the excitation energies. The logarithmic intensity scale of the inset highlights the step intensity onset of the PFY signal with comparison to the TEY threshold.
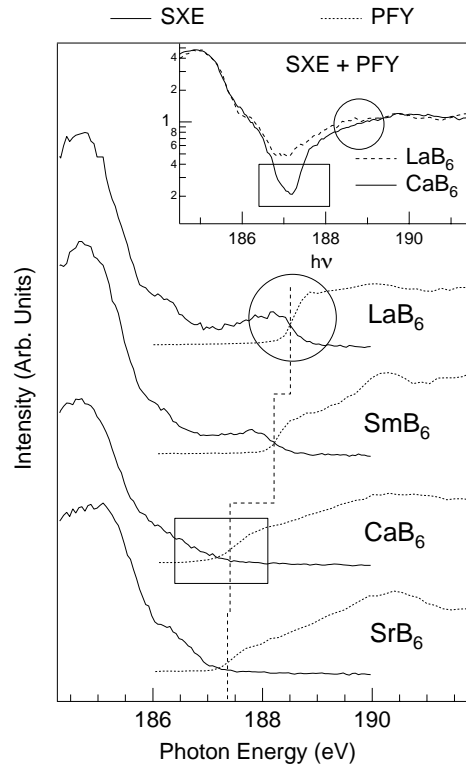


Figure 2. B K-edge SXE and PFY spectra for various hexaborides. The dashed line indicates the half-height energy position of the PFY threshold. Inset: Logarithmic intensity scale comparison of the total DOS, i.e. sum of emission and absorption, for $CaB_6$ and $LaB_6$ with the valence band edge of the DOS aligned.

Valence band emission spectra, shown in Fig. 1(b) were acquired at selected photon energies indicated by arrows in Fig. 1. An elastic peak present in the emission spectra is resonantly enhanced at the B 1s→2p absorption peak and is used for calibration of the SXE energy scale to that of TEY and PFY spectra. Excitation at the selected peaks in the PFY/TEY spectra and far above threshold show similar valence band emission profiles with small variations in the relative intensities of at least six discernable peaks and shoulders. Threshold excitation on the other hand produces much larger variation in the relative intensities (and energies) of the different valence emission peaks (discussed in the next section). The elastic peak is also observed to be enhanced at threshold, thus providing a distinct marker for the location of $E_F$. The non-threshold SXE spectra, on the other hand, exhibit a strong non-metallic decay of intensity approaching $E_F$ and no distinct onset, in contrast to the PFY spectrum.

Fig. 2 shows a comparison of SXE/PFY spectra for two divalent hexaborides $SrB_6$ and $CaB_6$, and for mixed-valent $SmB_6$ and trivalent $LaB_6$, which contain 0.6 and 1 conduction electrons/formula unit, respectively. The PFY spectra have been normalized to have the same intensity far above threshold, while the SXE spectra have been normalized to have the same maximum amplitude. The overall PFY intensities were then scaled so that the SXE and PFY intensities for $LaB_6$ match at threshold. Within experimental resolution, a common SXE/PFY threshold occurs for $SmB_6$ and for $LaB_6$, as expected for simple metals. The increases in photon energy and intensity of the thresholds of $SmB_6$ and $LaB_6$ relative to the divalent systems and to each other are consistent with their differing conduction band fillings. In great contrast, for the divalent hexaborides, the strong decay of SXE intensity to its threshold and the weak PFY intensity at its threshold preclude the two spectra having a common onset.

The inset to Fig. 2 presents a more detailed comparison of $CaB_6$ and $LaB_6$ in which the SXE and PFY spectra have been summed and can be discussed as the boron partial DOS. In addition the $LaB_6$ spectrum has been shifted +0.3 eV, after summing, to align its valence band (185-186.5 eV) to that of $CaB_6$. The key motivation for this comparison is that apart from band filling, LDA calculations predict nearly identical total DOS for the divalent and trivalent systems. For $LaB_6$ the emission and absorption spectra meet smoothly so that the crossover place entirely disappears upon summing (see circles), whereas for $CaB_6$ a distinct dip remains over $\approx$1 eV around 187 eV (see rectangles). This distinct discrepancy immediately tells us that the band structures in the vicinity of the boron valence band maximum for $CaB_6$ and $LaB_6$ are different. The interpretation of this bulk-sensitive measurement as a band gap in the divalent hexaborides is strongly supported by the k-dependent view from ARPES which shows a >1 eV band gap in $CaB_6$ at the X-point in contrast to a 0.2 eV *overlap* of the same two bands in $LaB_6$ [9]. Additional analyses of the overall boron DOS bandwidth and energy centroid, and of threshold-excited SXE spectra provide complementary evidence of the bulk divalent band gap [10].

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